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N^1,N^1-Dimethyl-N^5-dithiocarboxybiguanide

Tetsuzo Ito,* Hiroshi Ohki and Takayuki Suyama

Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, Japan

Correspondence e-mail: ito@chem.kanagawa-it.ac.jp

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(N–C) = 0.003 Å
R factor = 0.033
wR factor = 0.037
Data-to-parameter ratio = 9.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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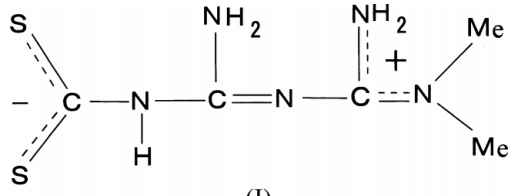
In the title compound, $C_5H_{11}N_5S_2$, the molecule adopts a zwitterionic structure. No H atoms are bonded to the dithiocarboxy S atoms nor to the N atom at the 3-position (N^3), but the two imino groups in the biguanide moiety are converted to amino groups. The molecule consists of two planar moieties sharing atom N^3; the dihedral angle between them is 58.0 (1)°.

Comment

In the study of reactions of 4,6-diamino-2*H*-1,3,5-thiadiazine-2-thione with several amines, the title compound, (I), was obtained and its probable structural formula was assigned (Suyama *et al.*, 1993). However, some ambiguities concerning the H-atom positions remained. In this study, the crystal structure of (I) has been determined, confirming the zwitterion structure (Fig. 1 and Table 1), which was suggested by Suyama *et al.* (1993). The intermolecular S1···N3, S2···N2 and S2···N4 distances (Table 2) are relatively short, with an average distance of 3.466 (9) Å; this appears to indicate the existence of electrostatic interactions between neighbouring molecules.



(I)

The molecule (I) consists of two planar moieties which share atom N3; plane 1 consists of atom N3 and the nine atoms to the left of it in Fig. 1, while plane 2 consists of atom N3 and the remaining seven atoms, excluding the six methyl H atoms.

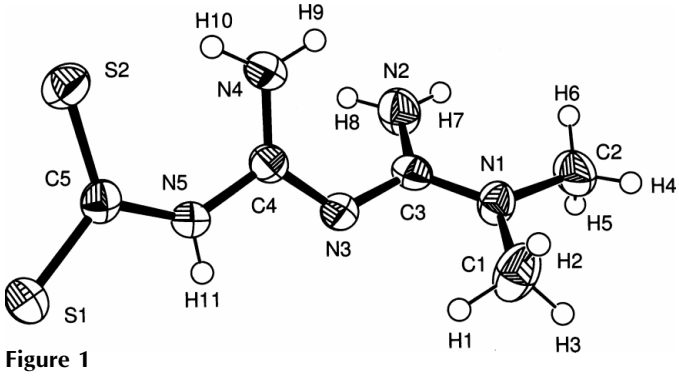


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids.

Best-plane calculations (Ito, 1982) performed without the H atoms, showed that the maximum deviations from best planes were 0.073 (2) Å and 0.060 (3) Å for atoms N3 of planes 1 and 2, respectively. The C5—S1 and C5—S2 bond distances are approximately the same, with an average distance of 1.690 (4) Å, corresponding to a bond order of 1.5. Therefore, the C═S double bond resonates between the two canonical structures. The N1—C1 and N1—C2 bond distances of 1.461 (3) and 1.457 (3) Å, respectively, can be regarded as single bonds, since the typical N—C and N═C bond distances are 1.47 and 1.25 Å, respectively. The N1—C3 and N2—C3 bond distances are 1.320 (3) and 1.335 (3) Å, respectively, suggesting conjugation in this part of the molecule.

Experimental

4,6-Diamino-2*H*-1,3,5-thiadiazine-2-thione (25 g) was suspended in dimethylformamide (DMF, 47 ml); dimethylamine (7.2 ml) was then added to the suspension, which changed to an orange-coloured solution. By stirring the solution for 10 min, a powder of (I) precipitated. Recrystallization from an aqueous DMF solution at 273 K gave yellow prismatic crystals of (I).

Crystal data

$C_5H_{11}N_5S_2$
M_r = 205.33
Monoclinic, $P2_1/n$
a = 7.979 (2) Å
b = 11.888 (3) Å
c = 10.618 (2) Å
β = 111.21 (1)°
V = 938.9 (4) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 15.2–16.3°
μ = 0.52 mm^{-1}
T = 296 K
Prism, yellow
0.39 × 0.39 × 0.32 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.799, T_{max} = 0.846
2419 measured reflections
2158 independent reflections
1517 reflections with $I > 3\sigma(I)$
R_{int} = 0.001
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 12$
3 standard reflections
every 150 reflections
intensity decay: 0.1%

Refinement

Refinement on F
R = 0.033
wR = 0.037
S = 1.71
1517 reflections
153 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C5	1.686 (2)	N3—C3	1.349 (3)
S2—C5	1.694 (2)	N3—C4	1.305 (3)
N1—C1	1.461 (3)	N4—C4	1.317 (3)
N1—C2	1.457 (3)	N5—C4	1.390 (3)
N1—C3	1.320 (3)	N5—C5	1.383 (3)
N2—C3	1.335 (3)		
C3—N3—C4	123.1 (2)	S1—C5—S2	122.9 (1)
C4—N5—C5	133.5 (2)		
C4—N3—C3—N1	136.7 (3)	C3—N3—C4—N5	169.4 (3)

Table 2
Contact distances (Å).

S1···N3^{i}	3.473 (2)	S2···N4^{iii}	3.448 (2)
S2···N2^{ii}	3.478 (3)		

Symmetry codes: (i) $2-x, -y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were located in difference Fourier syntheses and refined isotropically. The C—H and N—H bond lengths are 0.90 (3)–0.97 (3) and 0.78 (2)–0.89 (3) Å, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *CrystalStructure*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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